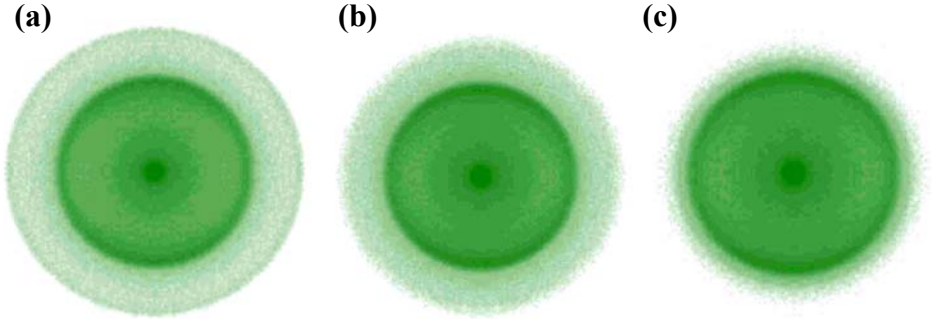
Time-resolved Photoelectron Imaging Studies of Electron Thermalization Dynamics in Size-selected Mercury Cluster Anions

Daniel M. Neumark, University of California, Berkeley, DMR-0139064

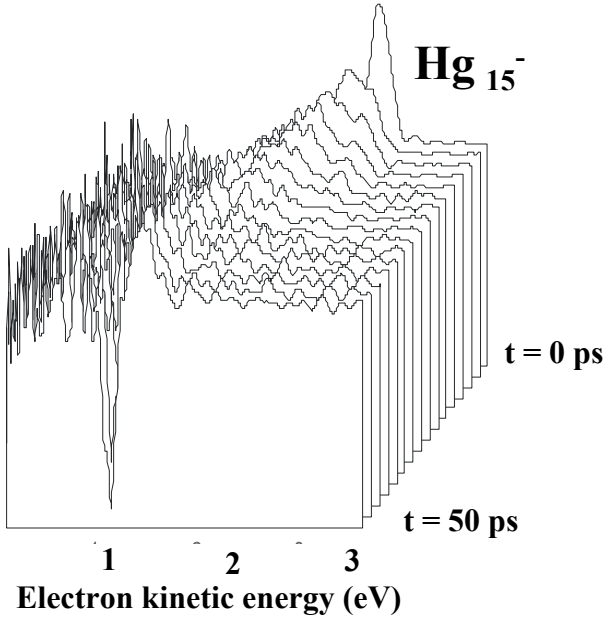
Finite cluster studies present the opportunity to trace the evolution of physical properties from the molecular to bulk, changes arising generally from alteration of bonding-type with size. Mercury, a noble metal possessing a filled 6*s* atomic sublevel, exhibits a range of cluster bonding types ranging from weak attraction to covalent to metallic as band structure slowly develops with size.

The addition of an excess electron accesses the empty 6*p* band in the neutral counterpart and is readily detached at visible to near-UV wavelengths. We examine time-dependent relaxation of the excess 6*p* electron via time-delayed photodetachment following infrared excitation towards determining size-dependent trends in electronic-to-vibrational relaxation. Trends in these relaxation rates within various size-regimes should reflect the nature of bonding, while time-dependent energetics should reveal detailed information regarding the character of these bonding regimes.



Time-resolved photoelectron images of Hg_{15}^- taken with 800 nm excitation, 400 nm detachment and delays of (a) 0 ps; (b) 8 ps; (c) 62 ps. Images are a 2D projection of a 3D-photodetachment distribution and are reconstructed to obtain photoelectron spectra.

Background-subtracted photoelectron spectral progression of Hg_{15}^- from 0 to 50 ps. Relaxation is reflected through decay and dispersion of the initial feature followed by long-time growth of a low kinetic energy feature.



Understanding the evolution of material properties between the molecular and bulk motivates theory and experimentation in cluster science, currently a hot region in chemical physics owing to a dearth of knowledge concerning this realm of matter. Experimentally, finite-sized cluster studies permit the step-wise examination of material properties between the micro- and macroscopic regimes, and have been used, for example, to establish semiconductor-to-metallic transitions through electronic band gap closure as well as to hone in on more subtle van der Waals-to-covalent bonding transitions.

The experiments considered here, undertaken within the Neumark Group in the College of Chemistry at UC Berkeley in collaboration with Professor Ori Cheshnovsky at Tel Aviv University, are designed to approach these problems through use of time-resolved techniques, whereby energetic excitations within a cluster are subsequently probed in order to examine relaxation timescales and mechanisms in a similar step-size cluster approach. These experiments are performed on finite mercury cluster anions (Hg_n^-, $n>3$), which are suspected theoretically to undergo dramatic bonding type alteration (van der Waals-to-covalent) at relatively small sizes (n=13-20). These experiments benefit from the negative charge based on (a) the size-selection readily achieved with charged particles through mass spectrometry, and (b) the single-occupancy of the 6*p* band of these clusters (these clusters possess a nominal $(6s)^{2n}(6p)^1$ occupancy), reducing the complexity of probed dynamics by excluding the effects of electron-electron interaction.

The excess electron is pumped at infrared wavelengths to higher levels of electronic excitation while its relaxation dynamics are probed subsequently through photodetachment of the same electron. Photodetachment produces a 3D photoelectron distribution cylindrically symmetric with respect to the detachment laser polarization. In time-resolved photoelectron imaging this distribution is 'pancaked' onto a 2D detector with the 3D distribution subsequently reconstructed. Thus one obtains both photoelectron energy and angular distributions finger-printed by participating energy levels of initiated dynamics at a given excitation-detachment delay.

The progression of images displayed exhibits a relaxation progression, whereby the outer feature, arising subsequent to excitation, shrinks with time – an indication of lessening photodetachment kinetic energy. The spectral progression displayed highlights these changes, where detachment from unexcited electrons has been removed. This shows that initial excitation at first disperses towards lower energies, recollecting at a lower energy at long times. An increase of this relaxation timescale and a change in the photodetachment intensity at intermediate times with size within a narrow window of clusters sizes (11-18) have been observed. Further investigation pursues the idea that these alterations should reflect changes in bonding type with cluster size.

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Education:

Two graduate students (Arthur Bragg and Aster Kammrath) and one postdoctoral fellow (Jan Verlet) contributed to this work. Aster Kammrath (2002-present), received an xxxxxx fellowship. Arthur Bragg (2000-present) received an NSF predoctoral fellowship for 1999-2002.

Previous project members contributing to our on-going research program include Alison Davis (grad, 1997-2002), Roland Wester (postdoc, 2000-2002), and Mason Guffey (undergrad, 2000-present). Alison Davis received her Ph.D. in 2002, was an NSF predoctoral fellow from 1997-2000, and is currently employed at Intel in Portland, OR. Mason Guffey will graduate in 2003.

Outreach:

This work has been undertaken in collaboration with Professor Ori Cheshnovsky, Tel Aviv University, and is jointly funded with a U.S.-Israeli Binational research grant.